Effect of increasing NCO/OH molar ratio on the physicomechanical and thermal properties of isocyanate terminated polyurethane prepolymer

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Abstract

The study investigates the effect of increasing NCO/OH molar ratio on the physico-mechanical and thermal properties of isocyanate terminated polyurethane prepolymer. The prepolymer was prepared using methylene diphenyl diisocyanate and difunctional polypropylene glycol. The NCO/OH molar ratio has been varied from 1.2:1 to 3:1. The formation of the prepolymer was confirmed by FTIR spectroscopy. The results reveal that the viscosity, weight average molecular weight and curing time of the prepolymer decreased with increase in NCO/OH molar ratio. When NCO/OH molar ratio increased, the tensile strength of the polyurethane film increased, while percent elongation decreased due to increase in hard segment content. The glass transition temperature of the prepolymer decreased with increase in NCO/ OH molar ratio of the prepolymer.

Keywords: *Polyurethane Prepolymer, Viscosity, Molecular Weight, Curing Time, Glass Transition Temperature.*

1. Introduction

Polyurethanes are considered one of the most versatile class of polymers for numerous commercial applications such as coating, foams, adhesives, sealants, membranes, and elastomer as well as in many biomedical applications. The urethane linkage (- NH – COO-) in polyurethane is a result of reaction between diisocyanate's isocyanate (-NCO) group and a polyol's hydroxyl group (-OH). If a stoichiometric excess of diisocyanate is used, the resulting short urethane chain are NCO terminated and the product is called isocyanate terminated polyurethane prepolymer. The curing of the prepolymer takes place by reaction with water leading to crosslinked structure of poly (urethane-urea) polymer with evolution of carbon dioxide. The basic chemistry of the curing process is shown in Scheme I.
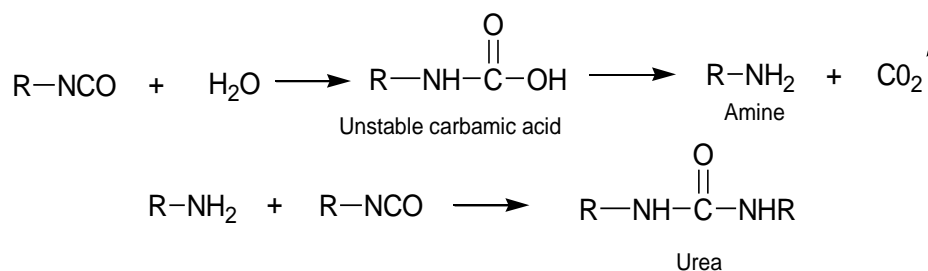
Scheme I: Curing Reaction of Isocyanate with Water

Polyurethanes have segmented structure consisting of alternative soft and hard blocks or segments and thus can be designed to have any properties to satisfy different material requirement. The type and concentration of hard and soft

segments plays a major role in regulating the morphology and physico-mechanical properties of polyurethane [1, 2].Soft segments are generally derived from a polyether or polyester polyol, whereas the isocyanates in conversion to urethane linkage form the hard segments. Usually the hard segments provide physical crosslinking through hydrogen bonding and filler like reinforcement to the soft segment, which plays a key role in imparting elasticity to polyurethane materials [1]. It has been reported in the literature that by varying the NCO/OH molar ratio, the microphase separation between hard and soft segment can be altered to obtain the desired properties of polyurethane. The literature reveals that NCO/OH molar ratio influences the viscosity buildup and onset of gelation of the prepolymer. Likewise in polyurethane coating it was observed that increase in isocyanate content yield more brittle and harder film and decrease in isocyanate content yield more flexible film.

Therefore, the NCO/OH molar ratio is regarded as an efficient way to regulate the morphology and properties of isocyanate terminated polyurethane prepolymer. The NCO/OH ratio is defined as the equivalent ratio between the materials containing NCO groups and those containing OH group.

So, in the present study focus was made for better understanding of the effect of increasing NCO/OH molar ratio on the physicomechanical and thermal properties of isocyanate terminated polyurethane prepolymer. The formation of the prepolymer was investigated by FTIR method and the physico-mechanical and thermal properties were investigated by Brookfield Viscometer, Gel Permeation Chromatography, and Tensile Test and Differential Scanning Calorimetry method. The mechanical properties was investigated by preparing polyurethane films and the curing time of the prepolymer was determined by noting its tack free time and set to touch time.

2. Experimental

2.1. Materials

Methylene diphenyl diisocyanate (MDI) was obtained from Sigma-Aldrich, USA. A white solid flakes (melt.pt. 40°C), it was used as such without further purification. Polypropylene glycol (PPG) was obtained from Sigma-Aldrich, USA. The polyol was vacuum dried for 2 hours at 80°C and kept overnight in molecular sieves prior to use to ensure that the material is free from moisture (less than 0.05%). Catalyst 2, 2´- Dimorpholinodiethyl ether (DMDEE) was procured from Degussa, Germany and used as such without any purification.

The properties of MDI and PPG used for the synthesis of polyurethane prepolymer are given in Table 1.

Table 1: Some Properties of MDI and PPG 1000 Used for Polyurethane Prepolymer Synthesis.

Property	MDI	PPG1000
Average functionality[a]	2.0	2.0
OH number (mg KOH/g)[a]	0.0	111
NCO content (wt%)[b]	33.8	0.0
Molecular weight (M_n(g/mol))[a]	250	1000
Viscosity 25°C, (cSt)[a]	50	150

[a] Information given by supplier

[b] Obtained by titration with di-n-butylamine

2.2. Synthesis of polyurethane (PU) prepolymer

The synthesis of PU prepolymer was carried out in a 5-necked glass reactor equipped with teflon stirrer, thermometer pocket, condenser and nitrogen gas inlet system. The MDI was melted in a beaker and poured into the reactor under nitrogen atmosphere. Inert atmosphere was maintained throughout the reaction so as to avoid the ingress of atmospheric moisture. The required amount of catalyst (0.25% of the whole reaction mixture) was then added followed by addition of PPG. The PPG was added part wise to the reactor. After that, the system was maintained at 60°C for 2 hours. The final prepolymer obtained was in the form of a yellow colored viscous liquid.

2.3. Preparation of polyurethane film

The polyurethane films were prepared by casting evaporation technique. Approximately 10% solution of polyurethane prepolymer in tetrahydrofuran was prepared and poured into a Teflon mould. It was then kept at room temperature, till all the solvent got evaporated and a transparent film was formed. The film obtained was of about 0.4 mm thickness.

2.4. Characterization

The properties of the synthesized prepolymers were investigated by the following methods:

The synthesis of the prepolymers was investigated by Fourier Transform Infrared Spectroscopy (FTIR) method. The FTIR spectra of the prepolymer was taken on an FTIR, Perkin Elmer Model 521 in the range of wave number from 400 cm^{-1} to 4000 cm^{-1} by coating 1mm thick layer of the prepolymer on a KBr pellet.

The isocyanate content of the prepolymer was determined as per ASTM D 2572-91. The isocyanate present in the prepolymer was reacted with an excess of di-n-butyl amine and then titrated with standard 0.1N HCl solution. Since a known amount of amine was added, the amine consumed by the prepolymer is due to the presence of free isocyanate which was determined. The data given are the average of three measurements.

Molecular weight of the prepolymer was determined by gel permeation chromatography using 2414 RI Detector (Make –Waters) and polystyrene as a standard. The samples were prepared in duplicate by dissolving 0.5% and 0.1% by wt of prepolymer in tetrahydrofuran (THF). THF was also used as a carrier solvent at the rate of 0.5 ml/min.

Dynamic viscosity of the prepolymer was determined by Brookfield viscometer DV Pro II (Brookfield Engineering Laboratories Inc, USA). The measurements were performed at 35 ± 1^oC at 12 rpm using spindle No.4.

The set to touch time of the prepolymer was determined according to ASTM D1640 – 03 (2009). A thin film (approx thickness 12.5µm) of PU prepolymer was coated on a glass plate. From time to time, the tip of a clean finger was lightly touched on the test film and immediately placed the fingertip on a piece of clean, clear glass plate. Observed, if any of the prepolymer was transferred to the glass plate. If no prepolymer was transferred, the time was noted as the set to touch time of the prepolymer. The test was carried out at $30\text{-}32^oC$ and relative humidity of 40-45%. An average of three measurements was taken as the result.

Tack-free time of the prepolymer was determined according to IS 101 (Part 3/Sec1) -1986. A thin film of the PU prepolymer was coated on a glass plate. The plate was then placed in one pan of a suitable balance and counterpoised it with weights. Placed a further weight of 2.25kg and press on the dried film surface of the plate with thumb till the two pans are balanced. Hold for one minute and then slowly release. If no sign of stickiness appears on the thumb, the time was noted and reported as tack-free time of the prepolymer. Temperature was maintained at $30\text{-}32^oC$ and relative humidity of 40-45%. The data given was the average of three measurements.

The glass transition temperature (T_g) of the prepolymer was determined by Differential Scanning Calorimetric (DSC) method. The DSC measurement was carried out under nitrogen atmosphere on a DSC – 2910 (TA instrument). The heating rate was maintained at 10^oC / min in the temperature range of -100^oC to 100^oC.

The tensile strength and percent elongation of the polyurethane films were measured in a Universal testing machine (Tinius Olsen, H5KL). The dimension of the test specimen was 10cm x 2cm x 0.04cm and the measurement was performed under load cell of 250N with a crosshead speed of 5mm/min at room temperature. The data taken are the average of three measurements.

3.   Results and discussion

3.1. FTIR analysis of the synthesized prepolymers

Fig. 1 shows the IR spectra's of the synthesized prepolymers at different NCO/OH molar ratio. All the synthesized prepolymer shows the characteristics absorption bands of polyurethanes except in the peak associated to NCO stretching which shows higher absorption area in case of higher NCO/OH molar ratio. It was observed that all the prepolymers possess the following characteristic absorption bands, urethane NH stretching at 3300cm^{-1}, bending at 1516cm^{-1}, methylene or alkyl group at 2974cm^{-1}, carbonyl group at 1700cm^{-1} and C-O-C stretching at 1100cm^{-1}. The strong characteristic absorption peak at 2272 - 2275cm^{-1} is associated with NCO stretching. Presence of NCO stretching band and all the above-mentioned peaks indicates formation of isocyanate terminated polyurethane prepolymer.

3.2. Physico-mechanical properties of the synthesized prepolymers

3.2.1. Isocyanate content

The isocyanate content of the prepolymer was determined by titrimetric method and it was observed that with increase in NCO/OH molar ratio, the isocyanate content of the prepolymer increases (Fig. 2).

3.2.2. Weight average molecular weight and Brookfield viscosity

The weight average molecular weight of the prepolymers was determined by GPC method using polystyrene standards. Fig.3 shows the effect of increasing NCO/OH molar ratio on weight average molecular weight of the prepolymer, while Fig.4 shows its effect on Brookfield viscosity of the prepolymer. The weight average molecular weight and consequently the Brookfield viscosity decreases with increase in NCO/OH molar ratio. When NCO/OH molar ratio

increases, the number of low molecular weight isocyanate segments per prepolymer molecule increases, which decreases the weight average molecular weight of the prepolymer and ultimately the Brookfield viscosity due to increase in free volume within the prepolymer molecule which increases the mobility of the polymer segments.
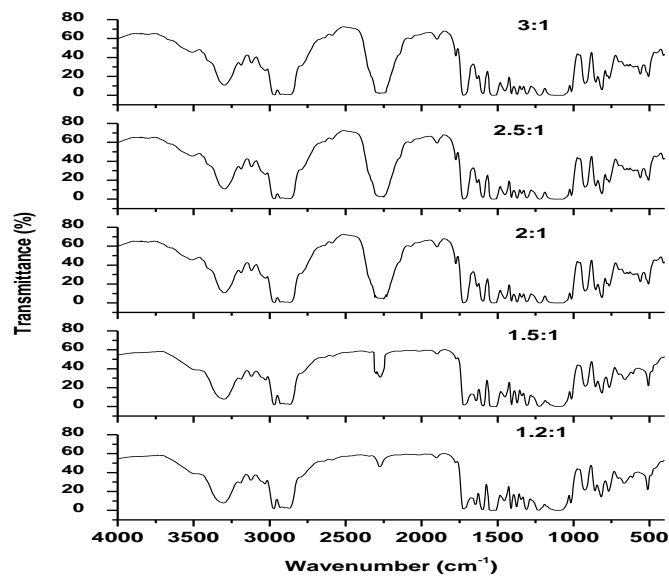

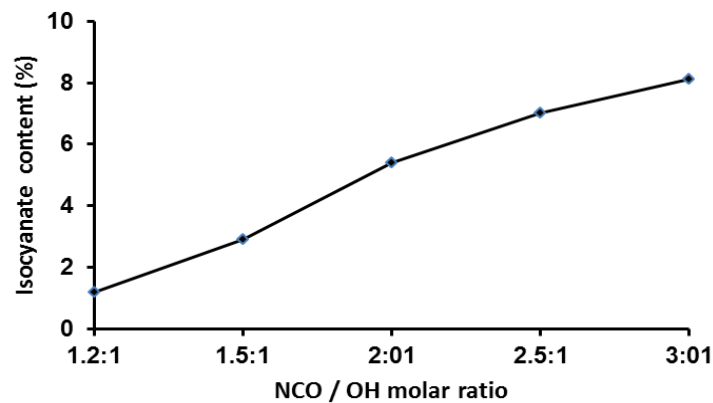**Fig. 1:** FTIR Spectra of the Synthesized Prepolymers at Different NCO/OH Molar Ratio

Fig. 2: Isocyanate Content of the Synthesized Prepolymer at Different NCO/OH Molar Ratio
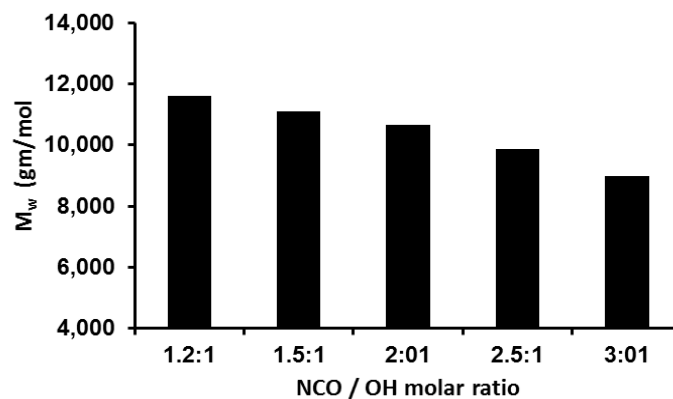

Fig. 3: Weight Average Molecular Weight (Mw) of the Synthesized Prepolymer at Different NCO/OH Molar Ratio
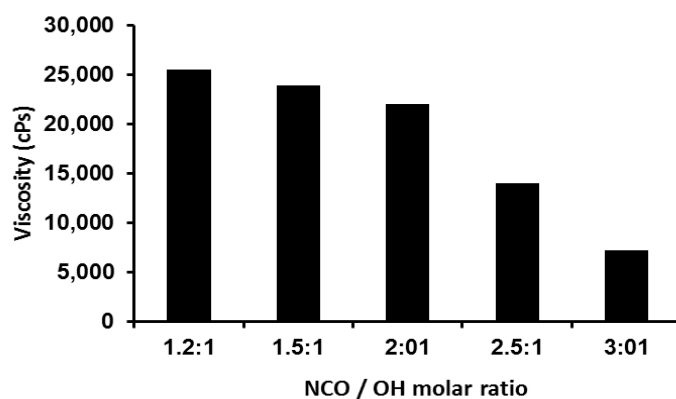
Fig. 4: Viscosity of the Synthesized Prepolymer at Different NCO/OH Molar Ratio

3.2.3. Curing time

The curing time of the synthesized prepolymers were investigated by determining its set to touch time and tack free time (Fig. 5). It was observed that the set to touch time and tack free time of the prepolymer decreases with increase in NCO/OH molar ratio. With increase in NCO/OH molar ratio, the isocyanate content of the prepolymer increases, thus generating more reactive NCO end groups which ultimately speed up the curing time of the prepolymer with water.
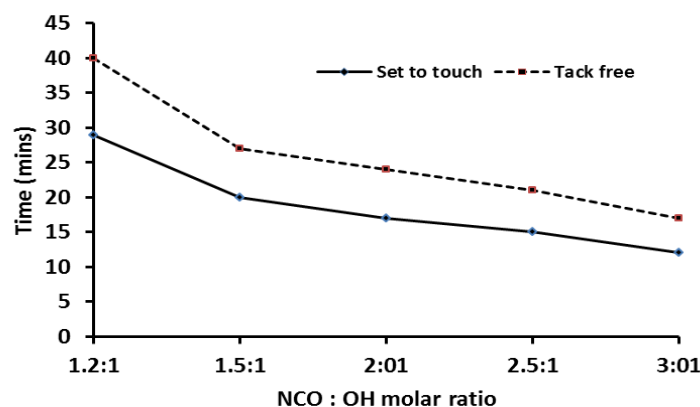

Fig. 5: Set to Touch Time and Tack Free Time of the Synthesized Prepolymer at Different NCO/OH Molar Ratio

3.2.4. Mechanical properties

To investigate the effect of increasing NCO/OH molar ratio on mechanical properties of the isocyanate terminated polyurethane prepolymers, polyurethane films were prepared by casting evaporation films. Fig. 6 shows the effect of increasing NCO/OH molar ratio on the tensile strength and percent elongation of the polyurethane film.
It was observed that on increasing the NCO/OH molar ratio, the tensile strength of the polyurethane film increases whereas the percent elongation decreases. This may be due to the fact that, with increasing NCO/OH molar ratio, hard segment content of the polymer increases. More hard segments allow more effective intermolecular hydrogen bonding between the segments [4]. This tends to increase the tensile strength and decreases the percent elongation of the polyurethane film with increase in NCO/OH molar ratio.

3.3. Thermal properties

The thermal properties of the synthesized polyurethane prepolymer were investigated by using the DSC technique (Fig. 7). For all the synthesized prepolymers, only one T_g was observed in our work. It can be seen from the thermograms that the T_g values of the prepolymer decreased with increasing NCO/OH molar ratio due to the decrease in weight average molecular weight of the prepolymer. The decrease in T_g is due to the increase in the number of short chain segments within the prepolymer with increase in NCO/OH molar ratio. The presence of more short chain segment increases the free volume within the polymer which ultimately increases the mobility of the polymer segments and decreases the T_g of the prepolymer.
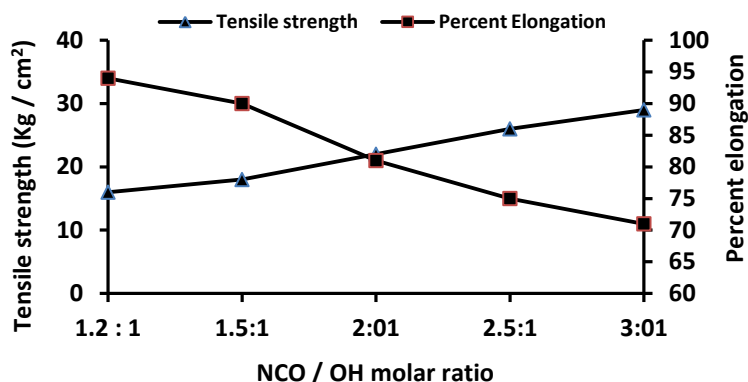
Fig. 6: Tensile Strength and Percent Elongation of the Polyurethane Films at Different NCO/OH Molar Ratio
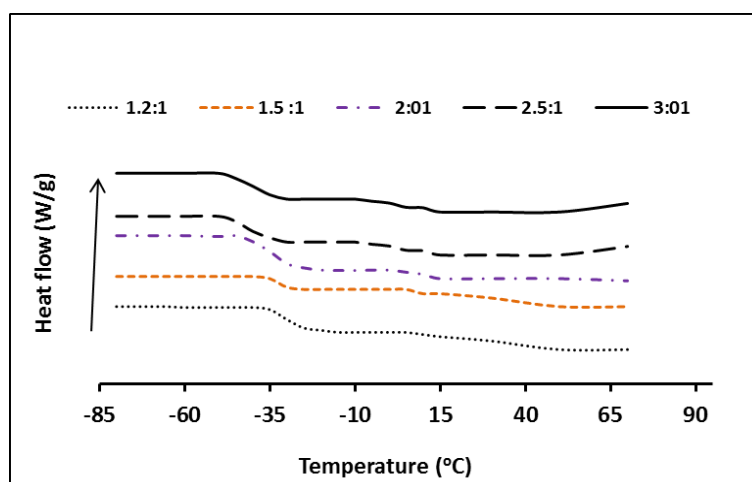

Fig. 7: DSC Thermograms of the Synthesized Prepolymers at different NCO/OH Molar Ratio

4. Conclusion

The findings of the study reveals that with increase in NCO/OH molar ratio, the viscosity, molecular weight and curing time of the isocyanate terminated polyurethane prepolymer decreases. The mechanical properties studied on polyurethane films shows that tensile strength increase, while percent elongation decreases with increase in NCO/OH molar ratio. The thermal analysis of the prepolymers shows that the glass transition temperature decreased with increase in NCO/OH molar ratio.

Acknowledgement

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